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(54) **HYDROXYMETHYL FURFURAL OXIDATION METHODS**

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4,897,497 A	1/1990	Fitzpatrick
4,977,283 A	12/1990	Leupold et al.
5,608,105 A	3/1997	Fitzpatrick
5,892,107 A	4/1999	Farone et al.
6,706,900 B2	3/2004	Grushin et al.
6,790,997 B2	9/2004	Eckert et al.
7,956,203 B2	6/2011	Grushin et al.
2003/0055271 A1	3/2003	Grushin et al.

#### FOREIGN PATENT DOCUMENTS

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DE	3826073 A1	7/1988
EP	0356703 A	3/1990
FR	2669636 A1	5/1992
GB	2188927 A	10/1987
JP	55049368 A	4/1980

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(52) **U.S. Cl.** ..... **549/489**

(58) **Field of Classification Search** ..... 549/483,  
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See application file for complete search history.

(56) **References Cited**

#### U.S. PATENT DOCUMENTS

3,326,944 A	6/1967	Lew
4,549,025 A	10/1985	Dalcanale et al.

#### OTHER PUBLICATIONS

Durst, *Experimental Organic Chemistry*, table 4.1, 1980, McGraw-Hill, Inc., p. 146-147, in 4 total pages including a cover sheet.\*

(Continued)

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(57) **ABSTRACT**

A method of oxidizing hydroxymethylfurfural (HMF) includes providing a starting material which includes HMF in a solvent comprising water into a reactor. At least one of air and O<sub>2</sub> is provided into the reactor. The starting material is contacted with the catalyst comprising Pt on a support material where the contacting is conducted at a reactor temperature of from about 50° C. to about 200° C. A method of producing an oxidation catalyst where ZrO<sub>2</sub> is provided and is calcined. The ZrO<sub>2</sub> is mixed with platinum (II) acetylacetonate to form a mixture. The mixture is subjected to rotary evaporation to form a product. The product is calcined and reduced under hydrogen to form an activated product. The activated product is passivated under a flow of 2% O<sub>2</sub>.

**10 Claims, 39 Drawing Sheets**

